1   On the Combination of TDDFT with Molecular Dynamics: New Developments

José L. Alonso, Alberto Castro, Pablo Echenique and Angel Rubio

José L. Alonso
Departamento de Física Teórica, Universidad de Zaragoza, Pedro Cerbuna 12, E-50009 Zaragoza (Spain); Instituto de Biocomputación y Física de Sistemas Complejos (BIFI), Universidad of Zaragoza, Mariano Esquillor s/n, E-50018 Zaragoza (Spain).
`alonso.buj@gmail.com`

Alberto Castro
Instituto de Biocomputación y Física de Sistemas Complejos (BIFI), Universidad of Zaragoza, Mariano Esquillor s/n, E-50018 Zaragoza (Spain).
`acastro@bifi.es`

Pablo Echenique
Instituto de Química Física "Rocasolano", CSIC, Serrano 119, E-28006 Madrid (Spain); Instituto de Biocomputación y Física de Sistemas Complejos (BIFI), Universidad of Zaragoza, Mariano Esquillor s/n, E-50018 Zaragoza (Spain); Departamento de Física Teórica, Universidad de Zaragoza, Pedro Cerbuna 12, E-50009 Zaragoza (Spain).
`echenique.p@gmail.com`

Angel Rubio
Nano-Bio Spectroscopy Group and ETSF Scientific Development Centre, Departamento de Física de Materiales, Universidad del País Vasco, E-20018 San Sebastián (Spain); Centro de Física de Materiales CSIC-UPV/EHU-MPC and DIPC, E-20018 San Sebastián (Spain); Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6 , D-14195 Berlin-Dahlem, Germany
`angel.rubio@ehu.es`

1.1   Introduction

In principle, we should not need the time-dependent extension of density-functional theory (TDDFT) for excitations, and in particular not for Molecular Dynamics (MD) studies: the theorem by Hohenberg and Kohn [Hohenberg 1964] teaches us that for any observable that we wish to look at (including dynamical properties or observables dependent on excited states) there is a corresponding functional of the ground-state density. Yet the unavailability of such magic functionals in many cases (the theorem is a non-constructive existence result) demands the development and use of the alternative exact

reformulation of quantum mechanics provided by TDDFT. This theory defines a convenient route to electronic excitations and to the dynamics of a many-electron system subject to an arbitrary time-dependent perturbation (discussed in previous chaters of this book). This is, in fact, the main purpose of inscribing TDDFT in a MD framework –the inclusion of the effect of electronic excited states in the dynamics. However, as we will show in this chapter, it may not be the only use of TDDFT in this context.

The term "Ab Initio Molecular Dynamics" (AIMD) has been exclusively identified in the past with the Car-Parrinello (CP) technique [Car 1985]. This method combines ground-state DFT with MD, providing an efficient reformulation of ground-state Born-Oppenheimer MD (gsBOMD) [Marx 2000]. However, the "AIMD" words have broader meaning, and should include all the possible MD techniques that make use of a first principles approach to tackle the many-electron problem. For example, Ehrenfest MD (EMD) can also be one AIMD scheme if TDDFT is used to propagate the electronic subsystem. This is the most common manner in which TDDFT and MD have been combined in the past: as a means to study fast out-of-equilibrium processes, typically intense laser irradiations or ionic collisions [Saalmann 1996, Saalmann 1998, Reinhard 1999, Kunert 2001, Castro 2004].

Nevertheless, there are other possibilities. In this chapter we review two recent proposals: In Section 1.2, we show how TDDFT can be used to design efficient gsBOMD algorithms [Alonso 2008, Andrade 2009] –even if the electronic excited states are in this case not relevant. The work described in Section 1.3 addresses the problem of mixed quantum-classical systems at thermal equilibrium [Alonso 2010].

1.2   Fast Ehrenfest Molecular Dynamics

Ehrenfest Molecular Dynamics (EMD) is a model for describing the evolution of a mixed quantum-classical system. The equations of motion are given by:

$$M_\alpha \frac{\mathrm{d}^2}{\mathrm{d}t^2} \boldsymbol{R}_\alpha(t) = -\langle \Phi(t)|\nabla_{\boldsymbol{R}_\alpha} \hat{H}_\mathrm{e}(\boldsymbol{R}(t),t)|\Phi(t)\rangle \,, \qquad (1.1)$$

$$\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}|\Phi(t)\rangle \qquad = \hat{H}(\boldsymbol{R}(t),t)|\Phi(t)\rangle \,, \qquad (1.2)$$

where $\Phi(t)$ is the state of the quantum subsystem (we will assume that this is a set of N electrons), and $\{\boldsymbol{R}_\alpha\}_{\alpha=1}^{N_\mathrm{nuc}}$ are the position coordinates of N_nuc classical particles (a set of N_nuc nuclei of masses M_α and charges z_α). The quantum (or *electronic*) Hamiltonian operator $\hat{H}_\mathrm{e}(\boldsymbol{R}, t)$ depends on these

classical coordinates, and is usually given by:

$$\hat{H}_{\mathrm{e}}(\boldsymbol{R},t) := \sum_{i=1}^{N} \frac{1}{2}\hat{p}_i^2 + \sum_{i,j<i} \frac{1}{|\hat{\boldsymbol{r}}_i - \hat{\boldsymbol{r}}_j|} + \sum_{\beta<\alpha} \frac{z_\alpha z_\beta}{|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|}$$
$$- \sum_{\alpha,i} \frac{z_\alpha}{|\boldsymbol{R}_\alpha - \hat{\boldsymbol{r}}_i|} + \sum_i v_{\mathrm{ext}}^{\mathrm{e}}(\hat{\boldsymbol{r}}_i,t) + \sum_\alpha v_{\mathrm{ext}}^{\mathrm{n}}(\boldsymbol{R}_\alpha,t)\,, \quad (1.3)$$

where $v_{\mathrm{ext}}^{\mathrm{e}}$ and $v_{\mathrm{ext}}^{\mathrm{n}}$ are external potentials acting on the electrons and nuclei, respectively [Echenique 2007]. Atomic units are used throughout the document in order to get rid of constant factors such as $\hbar$ or $1/4\pi\varepsilon_0$.

Given this definition, one can show that Eq. (1.1) can be rewritten as:

$$M_\alpha \frac{\mathrm{d}^2}{\mathrm{d}t^2}\boldsymbol{R}_\alpha(t) = - \int \mathrm{d}^3r\, n(\boldsymbol{r},t)\nabla_{\boldsymbol{R}_\alpha} v_0(\boldsymbol{r},\boldsymbol{R}(t))\,, \quad (1.4)$$

where

$$v_0(\boldsymbol{r},\boldsymbol{R}) := - \sum_\alpha \frac{z_\alpha}{|\boldsymbol{R}_\alpha - \boldsymbol{r}|}$$
$$+ \frac{1}{N} \sum_\alpha v_{\mathrm{ext}}^{\mathrm{n}}(\boldsymbol{R}_\alpha,t) + \frac{1}{N} \sum_{\beta<\alpha} \frac{z_\alpha z_\beta}{|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|}\,; \quad (1.5)$$

a result which is known as the "electrostatic force theorem" in the quantum chemistry literature [Levine 2000], and which is based in the fact that the gradient $\nabla_{\boldsymbol{R}_\alpha}\hat{H}_{\mathrm{e}}(\boldsymbol{R}(t),t)$ is a one-body local multiplicative operator (as far as the electrons are concerned), i.e., it is a sum of one-electron operators whose action amounts to a multiplication in real space [Eschrig 2003, Von Barth 2004].

Eq. (1.4) shows that the knowledge of the time-dependent electronic density $n(\boldsymbol{r},t)$ suffices to obtain the nuclear movement. This fact is the basis for TDDFT-based Ehrenfest MD (E-TDDFT): instead of solving Eq. (1.2), we solve the corresponding time-dependent Kohn-Sham system, which provides an approximation to $n(\boldsymbol{r},t)$:

$$\mathrm{i}\frac{\partial}{\partial t}\varphi_j(\boldsymbol{r},t) = -\frac{1}{2}\nabla^2\varphi_j(\boldsymbol{r},t) + v_{\mathrm{KS}}[n](\boldsymbol{r},t)\varphi_j(\boldsymbol{r},t)\,, \quad j=1,\dots,N\,, \quad (1.6)$$

being

$$v_{\mathrm{KS}}[n](\boldsymbol{r},t) := \sum_\alpha \frac{-z_\alpha}{|\boldsymbol{R}_\alpha(t) - \boldsymbol{r}|} + v_{\mathrm{H}}[n](\boldsymbol{r},t) + v_{\mathrm{xc}}[n](\boldsymbol{r},t) + v_{\mathrm{ext}}^{\mathrm{e}}(\boldsymbol{r},t)\,, \quad (1.7)$$

and

$$n(\boldsymbol{r},t) := 2\sum_{j=1}^{N} |\varphi_j(\boldsymbol{r},t)|^2\,, \quad (1.8)$$

where $v_{\mathrm{KS}}[n](\boldsymbol{r}, t)$ is the time-dependent Kohn-Sham potential, and $v_{\mathrm{H}}[n](\boldsymbol{r}, t)$ and $v_{\mathrm{xc}}[n](\boldsymbol{r}, t)$ are the Hartree and exchange-correlation potential, respectively. For simplicity, we assume an even number of electrons in a spin-compensated configuration.

The equations of motion for E-TDDFT (1.4, 1.6 and 1.8) can be derived from the following Lagrangian (assuming an adiabatic approximation for the exchange and correlation potential, as it is commonly done in practical implementations of TDDFT):

$$L_\mu[\varphi, \dot{\varphi}, \boldsymbol{R}, \dot{\boldsymbol{R}}] := \mu \frac{\mathrm{i}}{2} \sum_j \left(\langle \varphi_j | \dot{\varphi}_j \rangle - \langle \dot{\varphi}_j | \varphi_j \rangle \right)$$
$$+ \sum_\alpha \frac{1}{2} M_\alpha \dot{\boldsymbol{R}}_\alpha^2 - E_{\mathrm{KS}}[\varphi, \boldsymbol{R}] \,, \qquad (1.9)$$

for $\mu = 1$ (the reason for including this parameter μ will become clear in what follows). We use a dot to denote time-derivatives.

The term E_{KS} is the Kohn-Sham ground-state energy functional:

$$E_{\mathrm{KS}}[\varphi, \boldsymbol{R}] := 2 \sum_j \langle \varphi_j | \frac{\hat{p}^2}{2} | \varphi_j \rangle - \int \mathrm{d}^3 r \sum_\alpha \frac{z_\alpha}{|\boldsymbol{R}_\alpha - \boldsymbol{r}|} n(\boldsymbol{r})$$
$$+ \frac{1}{2} \int \mathrm{d}^3 r \, v_{\mathrm{Hartree}}[n](\boldsymbol{r}) n(\boldsymbol{r}) + E_{\mathrm{xc}}[n] + \sum_{\beta < \alpha} \frac{z_\alpha z_\beta}{|\boldsymbol{R}_\alpha - \boldsymbol{R}_\beta|} \,. \qquad (1.10)$$

Note that, when the time-dependent orbitals are introduced into this expression (as it is done in E-TDDFT), it becomes a functional of the Kohn-Sham orbitals at each time, and not a functional of the ground state density. Also, from here on, we assume that there are no external potentials $v_{\mathrm{ext}}^{\mathrm{e}}$ and $v_{\mathrm{ext}}^{\mathrm{n}}$, since they do not add anything to the following discussion.

It is worth remarking now that EMD differs from gsBOMD, and it is instructive to see in which way. We do so in the initial formulation of Eqs. (1.1) and (1.2) using the N-electron wavefunction for simplicity, i.e., we forget for a moment the TDDFT formalism.

To illustrate the main concepts we start by projecting the EMD equations into the adiabatic basis, formed at each nuclear configuration by the set of eigenfunctions of the electronic Hamiltonian:

$$\hat{H}_{\mathrm{e}}(\boldsymbol{R}) | \Psi_m(\boldsymbol{R}) \rangle = E_m(\boldsymbol{R}) | \Psi_m(\boldsymbol{R}) \rangle \,, \qquad (1.11)$$

$$|\Phi(t)\rangle = \sum_m c_m(t) | \Psi_m(\boldsymbol{R}(t)) \rangle \,. \qquad (1.12)$$

The result is:

$$M_\alpha \frac{\mathrm{d}^2}{\mathrm{d}t^2} \boldsymbol{R}_\alpha(t) = -\sum_m |c_m(t)|^2 \nabla_{\boldsymbol{R}_\alpha} E_m(\boldsymbol{R}(t))$$
$$- \sum_{mn} c_m^*(t) c_n(t) \left[E_m(\boldsymbol{R}(t)) - E_n(\boldsymbol{R}(t)) \right] \boldsymbol{d}_\alpha^{mn}(\boldsymbol{R}(t)) \quad (1.13)$$

$$\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t} c_m(t) = E_m(\boldsymbol{R}(t)) c_m(t) - \mathrm{i} \sum_n c_n(t) \left[\sum_\alpha \dot{\boldsymbol{R}}_\alpha \cdot \boldsymbol{d}_\alpha^{mn}(\boldsymbol{R}(t)) \right] \quad (1.14)$$

where the "non-adiabatic couplings" are defined as:

$$\boldsymbol{d}_\alpha^{mn}(\boldsymbol{R}) := \langle \Psi_m(\boldsymbol{R}) | \nabla_{\boldsymbol{R}_\alpha} \Psi_n(\boldsymbol{R}) \rangle . \quad (1.15)$$

If these are negligible, and we assume that the electronic system starts from the ground state ($c_m(0) = \delta_{m0}$), EMD reduces to gsBOMD:

$$M_\alpha \frac{\mathrm{d}^2}{\mathrm{d}t^2} \boldsymbol{R}_\alpha(t) = \nabla_{\boldsymbol{R}_\alpha} E_0(\boldsymbol{R}(t)) , \quad (1.16)$$
$$c_m(t) = \delta_{m0} . \quad (1.17)$$

Now, in order to integrate the gsBOMD equations, one can make use of ground-state DFT, since the only necessary ingredient is the ground-state energy $E_0(\boldsymbol{R}(t))$. One could thus precompute this hyper-surface, in order to propagate the nuclear dynamics *a posteriori*, or else only compute the energies at the $\boldsymbol{R}$ points visited by the dynamics (a procedure normally known as "on-the-fly"). However, Car and Parrinello [Car 1985] proposed an alternative, based on the following Lagrangian:

$$L_\lambda^{\mathrm{CP}}[\varphi, \dot{\varphi}, \boldsymbol{R}, \dot{\boldsymbol{R}}] := \lambda \frac{\mathrm{i}}{2} \sum_j \langle \dot{\varphi}_j | \dot{\varphi}_j \rangle + \sum_\alpha \frac{1}{2} M_\alpha \dot{\boldsymbol{R}}_\alpha^2$$
$$- E_{\mathrm{KS}}[\varphi, \boldsymbol{R}] + \sum_{ij} \Lambda_{ij} \left(\langle \varphi_i | \varphi_j \rangle - \delta_{ij} \right) . \quad (1.18)$$

Note the presence of a fictitious mass λ, and of a set of Lagrange multipliers Λ_{ij} associated to the constraints that keep the KS orbitals orthonormal along the evolution. The Car-Parrinello (CP) equations that stem from this Lagrangian are:

$$M_\alpha \frac{\mathrm{d}^2}{\mathrm{d}t^2} \boldsymbol{R}_\alpha(t) = -\nabla_{\boldsymbol{R}_\alpha} E_{\mathrm{KS}}[\varphi(t), \boldsymbol{R}(t))] , \quad (1.19)$$

$$\lambda \ddot{\varphi}_j(\boldsymbol{r}, t) = -\frac{1}{2} \nabla^2 \varphi_j(\boldsymbol{r}, t) + v_{\mathrm{KS}}[n](\boldsymbol{r}, t) \varphi_j(\boldsymbol{r}, t) + \sum_k \Lambda_{jk} \varphi_k(\boldsymbol{r}, t) , \quad (1.20)$$

$$\langle \varphi_i(t) | \varphi_j(t) \rangle = \delta_{ij} . \quad (1.21)$$

The first of these three sets of equation ensures that CP molecular dynamics (CPMD) is (approximately) equivalent to gsBOMD if the KS orbitals stay close to the ground-state ones; the second equation is an auxiliary, *fictitious* electronic propagation that enforces this proximity to the ground state for a certain range of values of the "mass" λ; whereas the last equation demands the constant orthonormality of the electronic orbitals. Another role of the fictitious mass *lambda* is to accelerate the fake electronic dynamics, and as a consequence to improve the numerical efficiency. This efficiency (in addition to the success of DFT in the calculation of total energies with chemical accuracy) has made of CPMD the method of choice for performing ab initio gsBOMD during the last decades.

When attempting simulations of very large systems, the calculations must be done using the massive parallel architectures presently available, therefore one must ensure a good scalability of the computational algorithms with respect to the number of processors and the size of the systems (ie. number of atoms). The CPMD technique at a given point has to face the problem posed by the need of orthonormalization, as required by Eq. (1.21). This is a very non-local process (regardless of the algorithm used), and therefore very difficult to parallelize efficiently. Linear-scaling methods and other approaches have been proposed recently [Kühne 2007] to improve the speed of the CP technique.

One possibility to circumvent the orthonormalization issue is to do E-TDDFT (which automatically conserves the orthonormality) instead of CPMD, for those cases in which the coupling to higher electronic excited states is weak, and therefore E-TDDFT is almost equivalent to gsBOMD. This fact was first realized by Theilhaber [Theilhaber 1992]. Unfortunately, the required time step for E-TDDFT is very small (two to three orders of magnitude smaller than the CPMD time-step), which makes it very inefficient computationally. The reason is that the simulation must follow the real electronic motion, which is very fast (in contrast to the fictitious electronic motion used in CPMD). In [Alonso 2008] and [Andrade 2009], however, it was shown how the time-step can be increased by modifying the μ parameter in the definition of the Lagrangian function given in Eq. (1.9), which for normal Ehrenfest dynamics should be $\mu = 1$.

For any μ, the equations of motion derived from this Lagrangian function are:

$$\mathrm{i}\mu\frac{\partial}{\partial t}\varphi_j(\boldsymbol{r},t) \ = -\frac{1}{2}\nabla^2\varphi_j(\boldsymbol{r},t) + v_{\mathrm{KS}}[n](\boldsymbol{r},t)\varphi_j(\boldsymbol{r},t)\,, \qquad (1.22)$$

$$M_\alpha\frac{\mathrm{d}^2}{\mathrm{d}t^2}\boldsymbol{R}_\alpha(t) = -\nabla_{\boldsymbol{R}_\alpha}E_{\mathrm{KS}}[\varphi(t),\boldsymbol{R}(t)]\,. \qquad (1.23)$$

The only difference with respect to E-TDDFT is the appearance of the μ parameter multiplying the time-derivative of the time-dependent KS equations. The most relevant features of this dynamics are:

1. The orthogonality of the time-dependent KS orbitals is automatically preserved along the evolution, so that there is no need to perform any orthonormalization procedure.
2. The "exact" total energy of the system, defined as

$$E = \frac{1}{2}\sum_\alpha M_\alpha \dot{\boldsymbol{R}}_\alpha^2 + E_{\mathrm{KS}}[\varphi, \boldsymbol{R}]\,, \tag{1.24}$$

   is also preserved along the evolution. Note that it is independent of μ and it coincides with the same exact energy that is preserved along the gsBOMD evolution. In contrast, the preserved energy in CPMD is given by:

$$E_{\mathrm{CP}} = E + \frac{1}{2}\lambda \sum_j \langle \dot{\varphi}_j | \dot{\varphi}_j \rangle\,, \tag{1.25}$$

   where E, given by Eq. (1.24), is now time-dependent. It can be seen how the new constant of motion E_{CP} actually depends on λ, which is the fictitious electronic mass introduced in the CP formulation.
3. If we consider Eq. (1.22), and write the left hand side as:

$$\mathrm{i}\mu\frac{\partial}{\partial t} = \mathrm{i}\frac{\partial}{\partial t_\mu}\,, \tag{1.26}$$

   the resulting equations can be seen as the standard Ehrenfest method in terms of a fictions time t_μ. This has the effect of scaling the TDDFT excitation energies by a $1/\mu$ factor. So we may open or close the electronic gap by using a μ smaller or larger than 1. Obviously, if $\mu \to 0$, then the gap becomes infinite, and we retrieve the adiabatic (gsBOMD) regime.
4. The second important effect of this time re-scaling is a change in the required time-step for the numerical propagation; if the time-step for the standard E-TDDFT equations is Δt, then the required time-step for the new dynamics is $\Delta t_\mu = \mu \Delta t$. In other words, the propagation will be μ times faster.
5. Taking into account the two previous points and recalling that the purpose of this modified Ehrenfest dynamics is to reproduce, albeit approximately, the gsBOMD results, it becomes clear that there is a tradeoff affecting the optimal choice for the value of μ: low values (but still larger than one) will give physical accuracy, while large values will produce a faster propagation. The optimal value is the maximum value that still keeps the system near the adiabatic regime. It is reasonable to expect that this value will be given by the ratio between the electronic gap and the highest vibrational frequency of the nuclei. For many systems, like some molecules or insulators, this ratio is large and we can expect large improvements with respect to standard Ehrenfest MD. For other systems, like metals, this ratio is small or zero and the new method will not work.
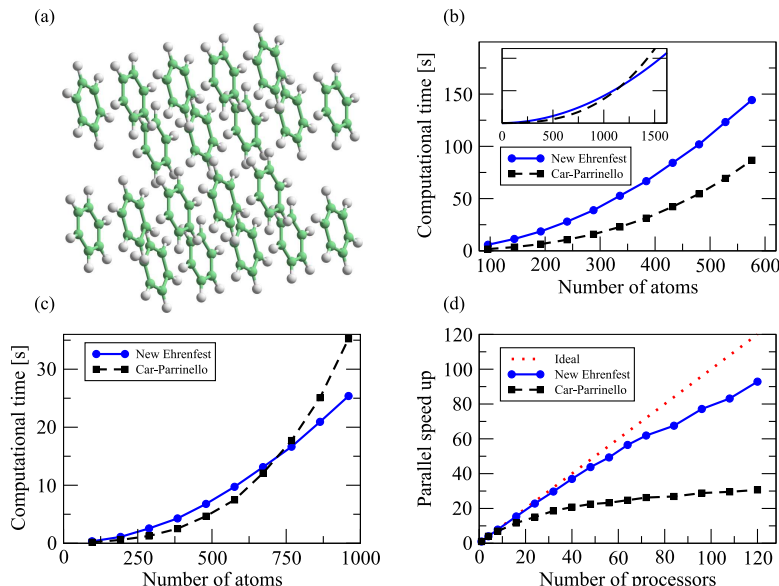
Fig. 1.1. (a) Scheme of the benzene molecule array. (b) Single processor computational cost for different system sizes. (inset) Polynomial extrapolation for larger systems. (c) Parallel computational cost for different system sizes. (d) Parallel scaling with respect to the number of processor for a system of 480 atoms. In both cases, a mixed states-domain parallelization is used to maximize the performance.

6. Regarding the scaling with the system size, the modified Ehrenfest dynamics evidently inherits the main advantage of the original one: since propagation preserves the orthonormality of the KS orbitals, it needs not be imposed and the numerical cost is proportional to $N_W N_C$ (with N_W the number of orbitals and N_C the number of grid points or basis set coefficients). For CPMD, a reorthogonalization has to be done each time step, so the cost is proportional to $N_W^2 N_C$. From these scaling properties, we can predict that for large enough systems the Ehrenfest method will be less costly than CP. For smaller systems, however, this gain will not compensate for the fact that the time-step, despite being increased by the μ factor, will still need to be one or two orders of magnitude smaller then the time-step utilized in CPMD.

Some numerical examples, performed with the octopus code [Marques 2003, Castro 2006], that give an idea of the performance of this modified Ehrenfest dynamics were shown in [Alonso 2008] and [Andrade 2009]. We reproduce here one case: the vibrational spectrum of an artificial benzene cristal (see Fig. 1.1). Essentially, the calculations consist of the time-propagation of the system, either with the standard CP technique or with the modified Ehrenfest dynamics, for an interval of time departing from a Boltzmann

distribribution of velocities at a given temperature. Then, the vibrational frequencies are obtained from the Fourier transform of the velocity autocorrelation function.

Panels (b) and (c) display the serial and parallel computational cost, respectively, of the two methods, defined as the computer time needed to propagate one atomic unit of time. In the serial case, it can be seen how for the system sizes studied, CP is more efficient; a different scaling can already be guessed from the curve; indeed, if these curves are extrapolated (inset), one can predict a crossing point where the new Ehrenfest technique starts to be advantageous. This is more patent in the parallel case, as can be seen in panel (c). Panel (d) displays the different scalability of the two methods: for a fixed system size, the system is equally divided in a variable number of processors, and the figure displays the different speed-ups obtained.

The key conclusion is that the lack of the orthonormalization step permits a new efficient parallelization layer, on top of the usual ones that are commonly employed in CPMD (domain decomposition, and Brillouin zone K-points): since the propagation step is independent for each orbital, it is natural to parallelize the problem by distributing the KS states among processors. Communication is only required once per time-step to calculate quantities that depend on a sum over states: the time dependent densities and the forces over the ions.

1.3   MD at finite electronic temperature

The previous section has addressed algorithmic alternatives to the solution of the gsBOMD equations (1.16) and (1.17). These represent the evolution of the classical nuclei, interacting all-to-all through the potential $E_0(\boldsymbol{R})$. The resulting dynamics can be used to calculate equilibrium averages at a given finite temperature, by assuming ergodicity and computing time averages over a number of trajectories, once the system has been appropriately coupled to a thermostat. The resulting marginal equilibrium density in the nuclear positions space being, in the canonical ensemble:

$$p_{\mathrm{gsBO}}(\boldsymbol{R}) = \frac{\mathrm{e}^{-\beta E_0(\boldsymbol{R})}}{\int \mathrm{d}\boldsymbol{R}' \mathrm{e}^{-\beta E_0(\boldsymbol{R}')}} \,, \tag{1.27}$$

with $\beta := 1/k_B T$, or $\beta := 1/RT$ if per-mole units are used.

However, this scheme ignores completely the dynamics of the electrons, by assuming that, even at a finite temperature, they are continuously tied to their ground state. This assumption is legitimate if the electronic gap is large compared to $k_B T$ at the temperature of interest. Indeed, in many physical, chemical or biological processes the dynamical effects arising from the presence of low lying electronic excited states have to be taken into account. For instance, in situations where the Hydrogen bond is weak, different states come close to each other and non-adiabatic proton transfer transitions

become rather likely at normal temperature [May 2004]. In these circumstances, the computation of ensemble averages cannot be based on a model that assumes the nuclei moving on the ground-state BO surface.

In the DFT realm, the inclusion of electronic excited states in the dynamics is very often done by working with partial occupation numbers to account for the electronic excitations [Grumbach 1994, Alavi 1994, Alavi 1995, Marzari 1997], ideally making use of temperature-dependent exchange and correlation functionals [Mermin 1965, Prodan 2010, Eschrig 2010]. This scheme is however tied to DFT, and is hindered by the difficulty of realistically approximating this functional. Other alternative options are Ehrenfest dynamics and surface hopping [Tully 1990] (for more on recent progress in non-adiabatic electronic dynamics in mixed quantum-classical dynamics, see, for example, [Zhu 2005]).

Recently, Alonso et al. [Alonso 2010] have proposed a new alternative, which can make use of the ability of TDDFT to compute electronic excited states. In the following, we make a summary of the new technique.

In order to arrive to a general quantum-classical formalism, and to a suitable expression for the quantum-classical equilibrium distribution that is considered to be the correct one in the literature, it is preferable in this case to follow the partial Wigner transformation route [Wigner 1932], as done by Ciccotti, Kapral and Nielsen [Kapral 1999, Nielsen 2001]. Let us assume a quantum system of two particles of masses m and M ($M > m$) living both in one dimension, whose canonical position and momentum operators are $(\hat{x},\hat{p})$ and $(\hat{X},\hat{P})$, respectively. The generalization to more particles and higher dimension is straightforward. Given an operator $\hat{A}$, its partial Wigner transform $\hat{A}_W$ with respect to the large-mass coordinate is defined as:

$$\hat{A}_W(X,P) := (2\pi\hbar)^{-1} \int \mathrm{d}z \; e^{\mathrm{i}Pz/\hbar} \langle X - z/2|\hat{A}|X + z/2\rangle \,. \qquad (1.28)$$

The operator $\hat{A}_W(X,P)$ acts on the Hilbert space of the *light* particle, and depends on the two real numbers (X,P). It is possible to reformulate all quantum theory in terms of these partial Wigner transforms; in particular, if the Hamiltonian for the two particles is given by:

$$\hat{H} = \frac{\hat{P}^2}{2M} + \frac{\hat{p}^2}{2m} + V(\hat{x},\hat{X}) \,, \qquad (1.29)$$

its transformation is:

$$\hat{H}_W(X,P) = \frac{P^2}{2M} + \frac{\hat{p}^2}{2m} + V(\hat{x},X) \,, \qquad (1.30)$$

i.e., one just has to substitute the quantum operators of the heavy particle by the real numbers (X,P).

If the state of the system is described by the density matrix $\hat{\rho}(t)$, its evolution will be governed by von Neumann's equation,

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho}(t) = -\frac{\mathrm{i}}{\hbar}\left[\hat{H},\hat{\rho}(t)\right] \,, \qquad (1.31)$$

which can be cast into its partial Wigner-transformed form:

$$\frac{\partial}{\partial t}\hat{\rho}_W = -\frac{i}{\hbar}\left(\hat{H}_W e^{\hbar\Lambda/2i}\hat{\rho}_W - \hat{\rho}_W e^{\hbar\Lambda/2i}\hat{H}_W\right),\qquad(1.32)$$

where Λ is the "Poisson bracket operator",

$$\Lambda := \frac{\overleftarrow{\partial}}{\partial P}\frac{\overrightarrow{\partial}}{\partial X} - \frac{\overleftarrow{\partial}}{\partial X}\frac{\overrightarrow{\partial}}{\partial P},\qquad(1.33)$$

and the arrows indicate the direction in which each derivative acts.

Note that up to now, this is an exact reformulation of quantum mechanics (no classical or semiclassical limit has been taken). However, this is also a convenient departure point to take the classical limit for the heavy particle. After an appropriate change of coordinates [Kapral 1999], if we retain only the first order terms in $\eta := (m/M)^{1/2}$, Eq. (1.32) is transformed into:

$$\frac{\partial}{\partial t}\hat{\rho}_W = -\frac{i}{\hbar}\left[\hat{H}_W, \hat{\rho}_W\right] + \frac{1}{2}\left(\{\hat{H}_W, \hat{\rho}_W\} - \{\hat{\rho}_W, \hat{H}_W\}\right),\qquad(1.34)$$

where $\{\cdot,\cdot\}$ is the Poisson bracket with respect to the canonical conjugate coordinates (X, P),

$$\{\hat{H}_W, \hat{\rho}_W\} := \frac{\partial\hat{H}_W}{\partial X}\frac{\partial\hat{\rho}_W}{\partial P} - \frac{\partial\hat{H}_W}{\partial P}\frac{\partial\hat{\rho}_W}{\partial X},\qquad(1.35)$$

and both $\hat{\rho}_W$ and $\hat{H}_W$ are functions of (X, P).

The equilibrium density matrix in the partial Wigner representation at the classical limit for the heavy particle, denoted by $\hat{\rho}_W^{eq}$ should be stationary with respect to the evolution at first order in $\eta := (m/M)^{1/2}$ in Eq. (1.34). If we use this property and expand the equilibrium density matrix in powers of η:

$$\hat{\rho}_W^{eq}(X, P) = \sum_{n=0}^{\infty}\eta^n\hat{\rho}_W^{eq\,(n)}(X, P),\qquad(1.36)$$

it can then be proved [Nielsen 2001] that the zero-th order term is given by:

$$\hat{\rho}_W^{eq\,(0)}(X, P) = \frac{1}{\mathcal{Z}}e^{-\beta\hat{H}_W(X,P)},\qquad(1.37)$$

with

$$\mathcal{Z} := \mathrm{Tr}_q\left[\int dX dP e^{-\beta\hat{H}_W(X,P)}\right],\qquad(1.38)$$

the symbol Tr_q meaning trace over the quantum degrees of freedom.

Note that (1.37) corresponds, at fixed classical variables (X, P), to the equilibrium density matrix *for the electronic states*. However, it is only an *approximation* to the true quantum-classical equilibrium density matrix, since it is not a stationary solution to the quantum-classical Liouvillian given

in Eq. (1.34). This distribution is often regarded, however, as the correct equilibrium distribution of the canonical ensemble for a mixed quantum-classical system [Mauri 1993, Parandekar 2005, Parandekar 2006, Schmidt 2008, Bastida 2007], and the average of observables is computed as:

$$\langle \hat{O}(\hat{x}, \hat{p}, X, P) \rangle = \mathrm{Tr_q} \int \mathrm{d}X \mathrm{d}P \hat{O}(\hat{x}, \hat{p}, X, P) \hat{\rho}_W^{\mathrm{eq}\,(0)}(X, P) \,. \qquad (1.39)$$

As mentioned, the careful analysis described in [Kapral 1999, Nielsen 2001], shows that this is a first order approximation in the square root of the quantum-classical mass ratio $\eta := (m/M)^{1/2}$, and therefore an acceptable approximation if this ratio is small.

In the remaining part of this chapter, and following [Alonso 2010], we will write a system of dynamic equations for the classical particles such that the equilibrium distribution in the space of classical variables is in fact given by Eq. (1.37). This is also a goal of surface hopping methods [Tully 1990], although it is not fully achieved since these methods do not exactly yield this distribution [Schmidt 2008]. We will do this by deriving a temperature-dependent effective potential for the classical variables, which differs from the ground-state potential energy surface (PES) used in gsBOMD. It is straight-forward, however, to write an equation that gives the expression for the effective potential in terms of this PES together with the BO PESs corresponding to the excited states of the electronic Hamiltonian. Despite this property, it is worth remarking that the approach described here is based on the assumption that the full system of electrons and nuclei is in thermal equilibrium at a given temperature, and not on the assumption that electrons immediately follow the nuclear motion (i.e., the adiabatic approximation), which is at the core of the BO scheme.

Let us assume that we are only interested in the average of observables that depend explicitly only on the degrees of freedom of the heavy, classical particle, $A = A(X, P)$. It is a matter of algebra (using Eqs. (1.37) and (1.39)) to prove that this average can be written as:

$$\langle A(X, P) \rangle = \frac{1}{\mathcal{Z}} \int \mathrm{d}X \mathrm{d}P A(X, P) \mathrm{e}^{-\beta H_{\mathrm{eff}}(X, P; \beta)} \,, \qquad (1.40)$$

where we have introduced an *effective* Hamiltonian H_{eff}, defined as:

$$H_{\mathrm{eff}}(X, P; \beta) := -\frac{1}{\beta} \ln \mathrm{Tr_q} \mathrm{e}^{-\beta H_W(X, P)} \,. \qquad (1.41)$$

The partition function $\mathcal{Z}$ can also be written in terms of the effective Hamiltonian:

$$\mathcal{Z} = \int \mathrm{d}X \mathrm{d}P \mathrm{e}^{-\beta H_{\mathrm{eff}}(X, P; \beta)} \,, \qquad (1.42)$$

Hence, the quantum subsystem has been "integrated out", and does not appear explicitly in the equations any more (of course, it has not disappeared,

being hidden in the definition of the effective Hamiltonian). In this way, the more complicated quantum-classical calculations have been reduced to a simpler classical dynamics with an appropriate effective Hamiltonian, which produces the same equilibrium averages of classical observables [Eq. (1.40)] as the one we would obtain using Eq. (1.37) in (1.39), and hence incorporates the quantum back-reaction on the evolution of the classical variables, at least at the level of equilibrium properties.

In the case of a molecular system, the total (partially Wigner transformed) Hamiltonian reads:

$$\hat{H}(\boldsymbol{R}, \boldsymbol{P}) = T_{\mathrm{n}}(\boldsymbol{P}) + \hat{H}_{\mathrm{e}}(\boldsymbol{R}), \tag{1.43}$$

where $\boldsymbol{R}$ denotes collectively all nuclear coordinates, $\boldsymbol{P}$ all nuclear momenta, $T_n(\boldsymbol{P})$ is the total nuclear kinetic energy, and $\hat{H}_{\mathrm{e}}(\boldsymbol{R})$ is the electronic Hamiltonian in Eq. (1.3), that includes the electronic kinetic term and all the interactions. The effective Hamiltonian, defined in Eq. (1.41) in general, is in this case of a molecular system given by:

$$H_{\mathrm{eff}}(\boldsymbol{R}, \boldsymbol{P}; \beta) := T_{\mathrm{n}}(\boldsymbol{P}) - \frac{1}{\beta} \ln \mathrm{Tr}_{\mathrm{q}} \mathrm{e}^{-\beta \hat{H}_{\mathrm{e}}(\boldsymbol{R})} =: T_{\mathrm{n}}(\boldsymbol{P}) + V_{\mathrm{eff}}(\boldsymbol{R}; \beta), \tag{1.44}$$

where the last equality is a definition for the *effective* potential $V_{\mathrm{eff}}(\boldsymbol{R}; \beta)$.

Now, making use of the adiabatic basis, defined in Eq. (1.11) as the set of all eigenvectors of electronic Hamiltonian $\hat{H}_{\mathrm{e}}(\boldsymbol{R})$, we can rewrite $V_{\mathrm{eff}}(\boldsymbol{R}; \beta)$ as:

$$V_{\mathrm{eff}}(\boldsymbol{R}; \beta) = E_0(\boldsymbol{R}) - \frac{1}{\beta} \ln \left[1 + \sum_{n>0} \mathrm{e}^{-\beta E_{n0}(\boldsymbol{R})} \right], \tag{1.45}$$

where $E_{\mathrm{n}0}(\boldsymbol{R}) := E_n(\boldsymbol{R}) - E_0(\boldsymbol{R})$. It is for the computation of these excitation energies that TDDFT can be employed. The proposed dynamics would be, therefore, *based* on TDDFT. Of course, any other many-electron technique can also be used.

This equation permits to see explicitly how the ground state energy E_0 differs from V_{eff}, and in consequence how a MD based on V_{eff} is going to differ from a gsBOMD. In particular, notice that $V_{\mathrm{eff}}(\boldsymbol{R}; \beta) \leq E_0(\boldsymbol{R})$, and compare the marginal probability density in the gsBOMD case in Eq. (1.27) to the one produced using the new dynamics:

$$p_{\mathrm{eff}}(\boldsymbol{R}) = \frac{\left(1 + \displaystyle\sum_{n>0} \mathrm{e}^{-\beta E_{n0}(\boldsymbol{R})} \right) \mathrm{e}^{-\beta E_0(\boldsymbol{R})}}{\displaystyle\int \mathrm{d}\boldsymbol{R}' \left(1 + \displaystyle\sum_{n>0} \mathrm{e}^{-\beta E_{n0}(\boldsymbol{R}')} \right) \mathrm{e}^{-\beta E_0(\boldsymbol{R}')}}. \tag{1.46}$$

Finally, note that to the extent that nuclei do not have quantum behavior near conical intersections or spin crossings, nothing prevents us to use this equation also in these cases.

The definition of the classical, effective Hamiltonian for the nuclear coordinates in Eq. (1.44) allows us now to use any of the well-established techniques available for computing canonical equilibrium averages in a classical system. Of course, since H_{eff} in Eq. (1.44) depends on T, any Monte Carlo or dynamical method must be performed at the same T that H_{eff} was computed in order to produce consistent results, given in this case by the convenient expression (1.40). For example, we could use (classical) Monte Carlo methods, or, if we want to perform MD simulations, we could propagate the stochastic Langevin dynamics associated to the Hamiltonian (1.44):

$$M_J \ddot{\boldsymbol{R}}_J(t) = -\boldsymbol{\nabla}_J V_{\text{eff}}(\boldsymbol{R}(t); \beta) - M_J \gamma \dot{\boldsymbol{R}}_J(t) + M_J \boldsymbol{\Xi}(t), \qquad (1.47)$$

where $\boldsymbol{\Xi}$ is a vector of stochastic fluctuations, obeying $\langle \Xi_i(t) \rangle = 0$ and $\langle \Xi_i(t_1) \Xi_j(t_2) \rangle = 2\gamma k_B T \delta_{ij} \delta(t_1 - t_2)$ which relates the dissipation strength γ and the temperature T to the fluctuations (fluctuation-dissipation theorem).

Indeed, it is well-known that this Langevin dynamics is equivalent to the Fokker-Planck equation for the probability density $W(\boldsymbol{R}, \boldsymbol{P})$ in the classical phase space [Van Kampen 2007]:

$$\frac{\partial W(\boldsymbol{R}, \boldsymbol{P}; t)}{\partial t} = \{H_{\text{eff}}(\boldsymbol{R}, \boldsymbol{P}; \beta), W(\boldsymbol{R}, \boldsymbol{P}; t)\}$$
$$+ \gamma \sum_J \partial_{\boldsymbol{P}_J}(\boldsymbol{P}_J + M k_{\text{B}} T \partial_{\boldsymbol{P}_J}) W(\boldsymbol{R}, \boldsymbol{P}; t). \qquad (1.48)$$

Any solution to Eq. (1.48) approaches at infinite time a distribution $W_{\text{eq}}(\boldsymbol{R}, \boldsymbol{P})$ such that $\partial_t W_{\text{eq}}(\boldsymbol{R}, \boldsymbol{P}) = 0$. This stationary solution is unique and equal to the Gibbs distribution, $W_{\text{eq}}(\boldsymbol{R}, \boldsymbol{P}) = \mathcal{Z}^{-1} \, \mathrm{e}^{-\beta H_{\text{eff}}(\boldsymbol{R}, \boldsymbol{P}; \beta)}$ [Van Kampen 2007]. Thus, the long-time solutions of Eq. (1.48), and hence those of Eq. (1.47) reproduce the canonical averages in Eq. (1.40). This property, which is also satisfied by other dynamics like the one proposed by Nosé [Nosé 1984, Nosé 1991] if the H_{eff} in Eq. (1.44) is used, comes out in a very natural way from the present formalism while it is yet unclear of other ab initio MD candidates for going beyond gsBOMD [Mauri 1993, Parandekar 2005, Schmidt 2008, Bastida 2007].

When would this new MD scheme be useful? The approach introduced in this section is particularly suited to the case of conical intersection or spin-crossing [Yarkony 1996], since it does not assume that the electrons or quantum variables immediately follow the nuclear motion, in contrast to any adiabatic approach. Another interesting application pertains the debated issue of quantum effects in proton transfer [Iyengar 2008]. It is a matter of current debate to what extent protons behave "quantum-like" in biomolecular systems (e.g. is there any trace of superposition, tunneling or entanglement in their behavior?). Recently, McKenzie and coworkers [Bothma 2010] have carefully examined the issue, and concluded that "tunneling well below the barrier only occurs for temperatures less than a temperature T_0 which is determined by the curvature of the PES at the top of the barrier." In

consequence, the correct determination of this curvature is of paramount importance.

The curvature predicted by the temperature-dependent effective potential introduced here is smaller than the one corresponding to the ground state PES, in the cases in which the quantum excited surfaces approach, at the barrier top, the ground state one. Therefore, T_0 would be smaller than that corresponding to the ground state PES (see Eq. (8) in [Bothma 2010]), and hence the conclusion in this reference "that quantum tunneling does not play a significant role in hydrogen transfer in enzymes" is reinforced by the results of the new dynamics.

Acknowledgments

References

Alavi, A., Kohanoff, J., Parrinello, M., Frenkel, D., 1994, "Ab Initio Molecular Dynamics with Excited Electrons", *Phys. Rev. Lett.*, vol 73, pp. 2599–2602.

Alavi, A., Parrinello, M., Frenkel, D., 1995, "Ab initio calculation of the sound velocity of dense hydrogen: implications for models of Jupiter", *Science*, vol 269, pp. 1252–1254.

Alonso, J. L., Andrade, X., Echenique, P., Falceto, Prada-Gracia, D., and Rubio, A., "Efficient Formalism for Large-Scale Ab Initio Molecular Dynamics based on Time-Dependent Density Functional Theory", *Phys. Rev. Lett.*, vol. 101, p. 096403.

Alonso, J. L., Castro, A., Echenique, P., Polo, V., and Rubio, A., and Zueco, D., 2010, "Ab Initio Molecular Dynamics on the Electronic Botzmann Equilibrium Distribution", *New J. Phys.*, vol. 12, p. 083064.

Andrade, X., Castro, A., Zueco, D., Alonso, J. L., Echenique, P., Falceto, F., and Rubio, A., "Modified Ehrennfest Formalism for Efficient Large-Scale ab initio Molecular Dynamics", *J. Chem. Theor. Comp.*, vol. 5, pp. 728–742.

Bastida, A., Cruz, C., Zúñiga, J., Requena, A., and Miguel, B., 2007, "The Ehrenfest method with quantum corrections to simulate the relaxation of molecules in solution: Equilibrium and dynamics", *J. Chem. Phys.* **126**, p. 014503,

Bothma, J. P., Gilmore, J. B., and McKenzie, R. H., 2010 "The role of quantum effects in proton transfer reactions in enzymes: quantum tunneling in a noisy environment?" *New. J. Phys.* **12**, p. 055002.

Car, R., and M. Parrinello, 1985, "Unified Approach for Molecular Dynamics and Density-Functional Theory", *Phys. Rev. Lett.*, vol. 55, pp. 2471–2471.

Castro, A., Marques, M. A. L., Alonso, J. A., Bertsch, G. F., and Rubio, A., 2004, "Excited states dynamics in time-dependent density functional theory", *Eur. Phys. J. D*, vol. 28, pp. 211–218.

Echenique, P., and Alonso, J. L., 2007, "A mathematical and computational review of Hartree-Fock SCF methods in Quantum Chemistry", *Mol. Phys.*, vol. 105, pp. 3057–3098.

Eschrig, H., 2003, *The Fundamentals of Density Functional Theory*, second edition, (Teubner, Leipzig).

Eschrig, H., 2010, "$T > 0$ ensemble-state density functional theory via Legendre transform", *Phys. Rev. B*, vol. 82, p. 205120.

Grumbach, M. P., Hohl, D., Martin, R. M., Car, R., "Ab initio molecular dynamics with a finite-temperature density functional", 1994, *J. Phys.: Condens. Matter*, vol. 6, pp. 1999–2014.

Hohenberg, P., and W. Kohn, 1964, "Inhomogeneous Electron Gas", *Phys. Rev.*, vol. 136, pp. B864–B871.

Iyengar, S. S., Sumner, I, and Jakowski J., 2008, "Hydrogen Tunneling in an Enzyme Active Site: A Quantum Wavepacket Dynamical Perspective", *J. Phys. Chem. B* **112**, pp. 7601–7613.

Kapral, R., and Ciccotti, G., 1999, "Mixed quantum-classical dynamics", *J. Chem. Phys.*, vol 110, pp. 8919–8929.

Kühne, T. D., Krack, M., Mohamed, F. R., and Parrinello, M., 2007, "Efficient and Accurate Car-Parrinello-like Approach to Born-Oppenheimer Molecular Dynamics", *Phys. Rev. Lett.*, vol. 98, p. 066401.

Kunert, T., and Schmidt, R., 2001, "Excitation and fragmentation mechanisms in ion-fullerene collisions", *Phys. Rev. Lett.*, vol. 86, pp. 5258–5261.

Levine, I. G., 2000, *Quantum Chemistry*, (Prentice-Hall).

Marques, M. A. L., Castro, A., Bertsch, G. F., and Rubio, A., 2003, "octopus: a first-principles tool for excited electron-ion dynamics", *Comp. Phys. Comm.*, vol. 151, pp. 60–78.

Castro, A., Appel, H., Oliveira, M., Rozzi, C. A., Andrade, X., Lorenzen, F., Marques, M. A. L., Gross, E. K. U., and Rubio, A., 2006, "octopus: a tool for the application of time-dependent density functional theory", *Phys. Stat. Sol. (b)*, vol. 243, pp. 2465–2488.

Marx, D., and Hutter, J., 2000, "Ab Initio Molecular Dynamics: Theory and Implementation", in *Modern Methods and Algorithms of Quantum Chemistry*, edited by J. Grotendorst, vol. 1 of *NIC Series*, pp. 301–449 (John von Neumann Institute for Computing, Jülich).

Marzari, N., Vanderbilt, D., and Payne, M. C., 1997, "Ensemble Density-Functional Theory for Ab Initio Molecular Dynamics of Metals and Finite-Temperature Insulators", *Phys. Rev. Lett.*, vol 79, pp. 1337–1340.

Mauri, F., Car, R., and Tosatti, E., 1993, "Canonical Statistical Averages of Coupled Quantum-Classical Systems", *Europhys. Lett.*, vol. 24, pp. 431–436.

May, V., and Kühne, O., 2004, *Charge and Energy Transfer Dynamics in Molecular Systems*, (Wiley-VCH, New York).

Mermin, N. D., 1965, "Thermal Properties of the Inhomogeneous Electron Gas" *Phys. Rev.*, vol 137, pp. A1441–A1443.

Nielsen, S., Kapral, R., and Ciccotti, G., 2001, "Statistical mechanics of quantum-classical systems", *J. Chem. Phys.*, vol 115, pp. 5805–5815.

Nosé, S., 19841, "A molecular dynamics method for simulations in the canonical ensemble", *Mol. Phys.* **52**, pp 255–268.

Nosé, S., 1991, "Constant Temperature Molecular Dynamics", *Prog. Theor. Phys. Suppl.* **103**, pp 1–46.

Parandekar, P. V., and Tully, J. C., 2005, "Mixed quantum-classical equilibrium", *J. Chem. Phys.*, vol. 122, p. 094102.

Parandekar, P. V., and Tully, J. C., 2006, "Detailed Balance in Ehrenfest Mixed Quantum-Classical Dynamics", *J. Chem. Theor. Comput.*, vol 2, pp. 217–228.

Prodan, E., 2010, "Raising the temperature on DFT", *Physics*, vol 3, p. 99.

Reinhard, P.-G., and Suraud, E., 1999, "On electron dynamics in violent cluster excitations", *J. Cluster Science*, vol. 10, pp. 239–270.

Saalmann, U., and Schmidt, R., 1996, "Non-adiabatic quantum molecular dynamics: basic formalism and case study", *Z. Phys. D*, vol 38, p. 153–163.

Saalmann, U., and Schmidt, R., 1998, "Excitation and relaxation in atom-cluster collisions", *Phys. Rev. Lett.*, vol 80, p. 3213–3216.

Schmidt, J. R., Parandekar, P. V., and Tully, J. C., 2008, "Mixed quantum-classical equilibrium: Surface hopping", *J. Chem. Phys.* **129**, p. 044104.

Theilhaber, J., 1992, "Ab initio simulations of sodium using time-dependent density-functional theory", *Phys. Rev. B* **46**, pp. 12990–13003.

Tully, J. C., 1990, "Molecular dynamics with electronic transitions", *J. Chem. Phys.*, vol. 93, pp. 1061–1071.

Van Kampen, N. G., 2007, *Stochastic Processes in Physics and Chemistry*, (Elsevier Science and Technology Books, Amsterdam).

Von Barth, U., 2004, "Basic Density-Functional Theory–an Overview", *Physica Scripta*, vol. T 109, p. 9.

Wigner, E., 1932, "On the Quantum Correction for Theormodynamic Equilibrium", *Phys. Rev.*, vol 40, pp. 749–759.

Yarkony, D. R., 1996, "Diabolical conical intersections", *Rev. Mod. Phys.*, vol 68, p. 985–1013.

Zhu, C., Jasper, A. W., and Truhlar, D. G., 2005, "Non-Born-Oppenheimer Liouville-von Neumann Dynamics. Evolution of a Subsystem Controlled by Linear and Population-Driven Decay of Mixing with Decoherent and Coherent Switching" *J. Chem. Theor. Comp.* **1**, pp. 527–540.